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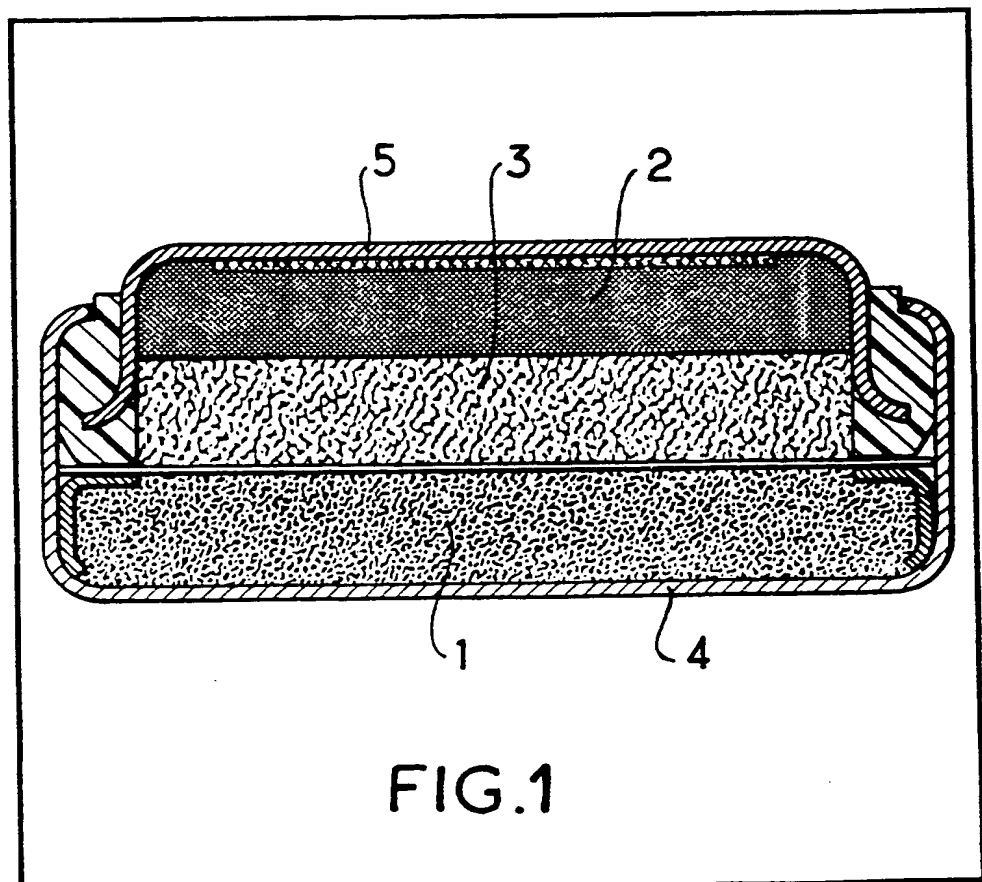
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(54) A lithium electric cell

(57) A lithium electric cell. Said electric cell includes a positive electrode (1) and a negative electrode (2) in contact with a liquid electrolyte impregnates in a separator (3). The positive electrode comprising an active compound whose general formula is  $\text{Li}_x\text{Fe}_2\text{S}_z$  with  $x$  lying between 0 and 2, and  $z$  being not less than 3. The active compound,  $\text{Li}_2\text{Fe}_2\text{S}_3$ , is prepared by heating to 800°C for about 6 h in a tube a stoichiometric mix of  $\text{Li}_2\text{CO}_3$  and  $\text{Fe}_2\text{O}_3$  while passing a  $\text{CS}_2$  loaded Ar stream through the tube.

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FIG.1

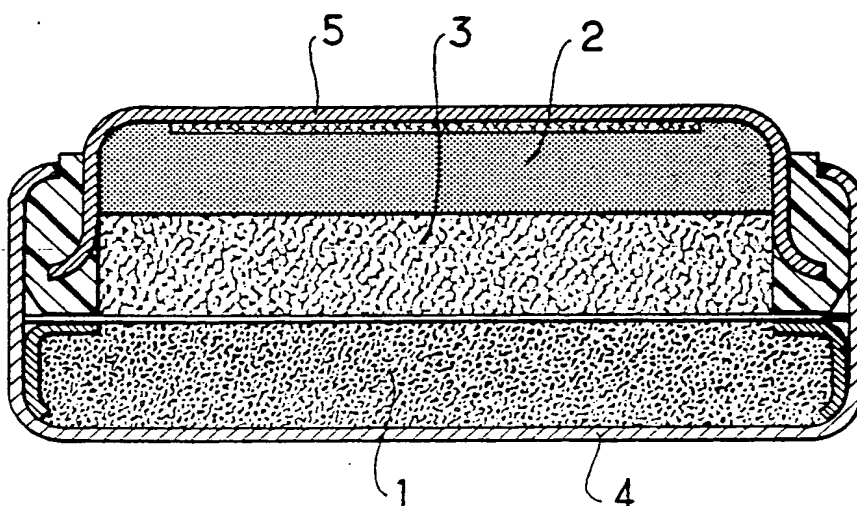


FIG. 2

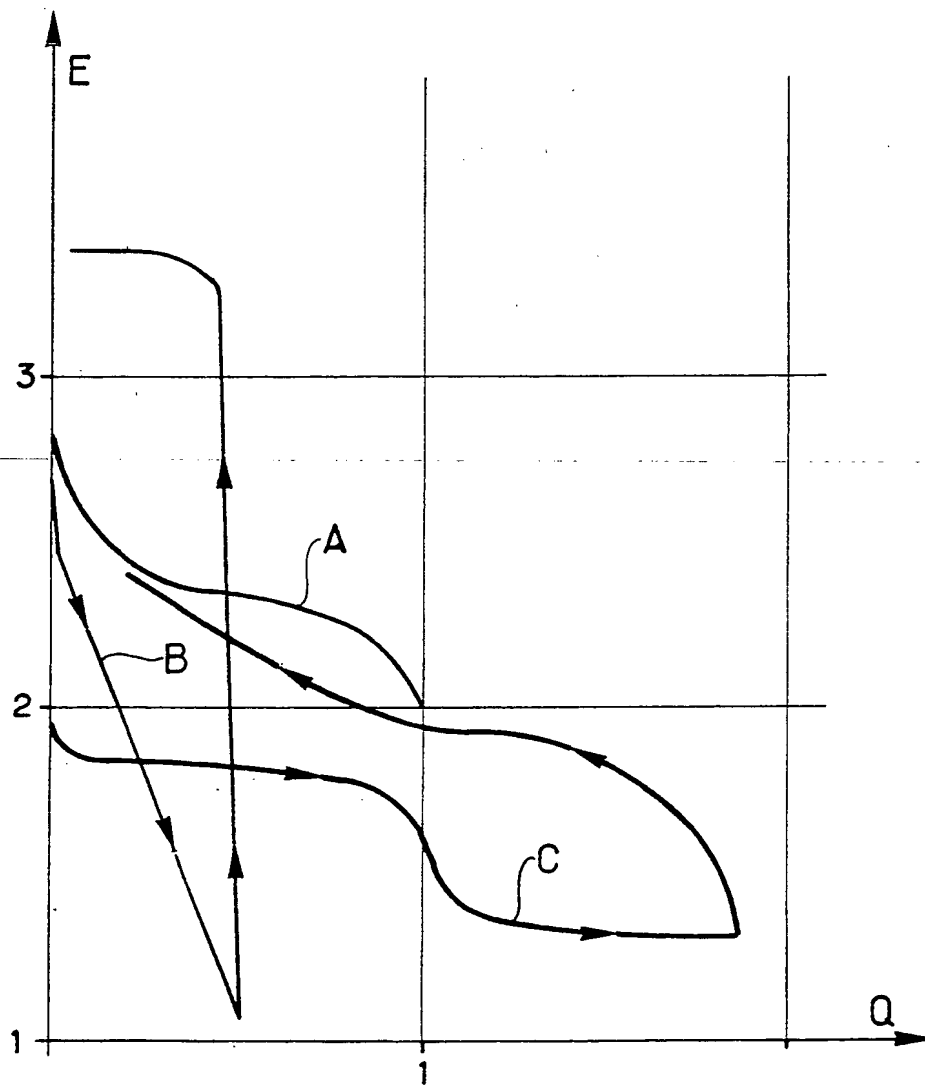
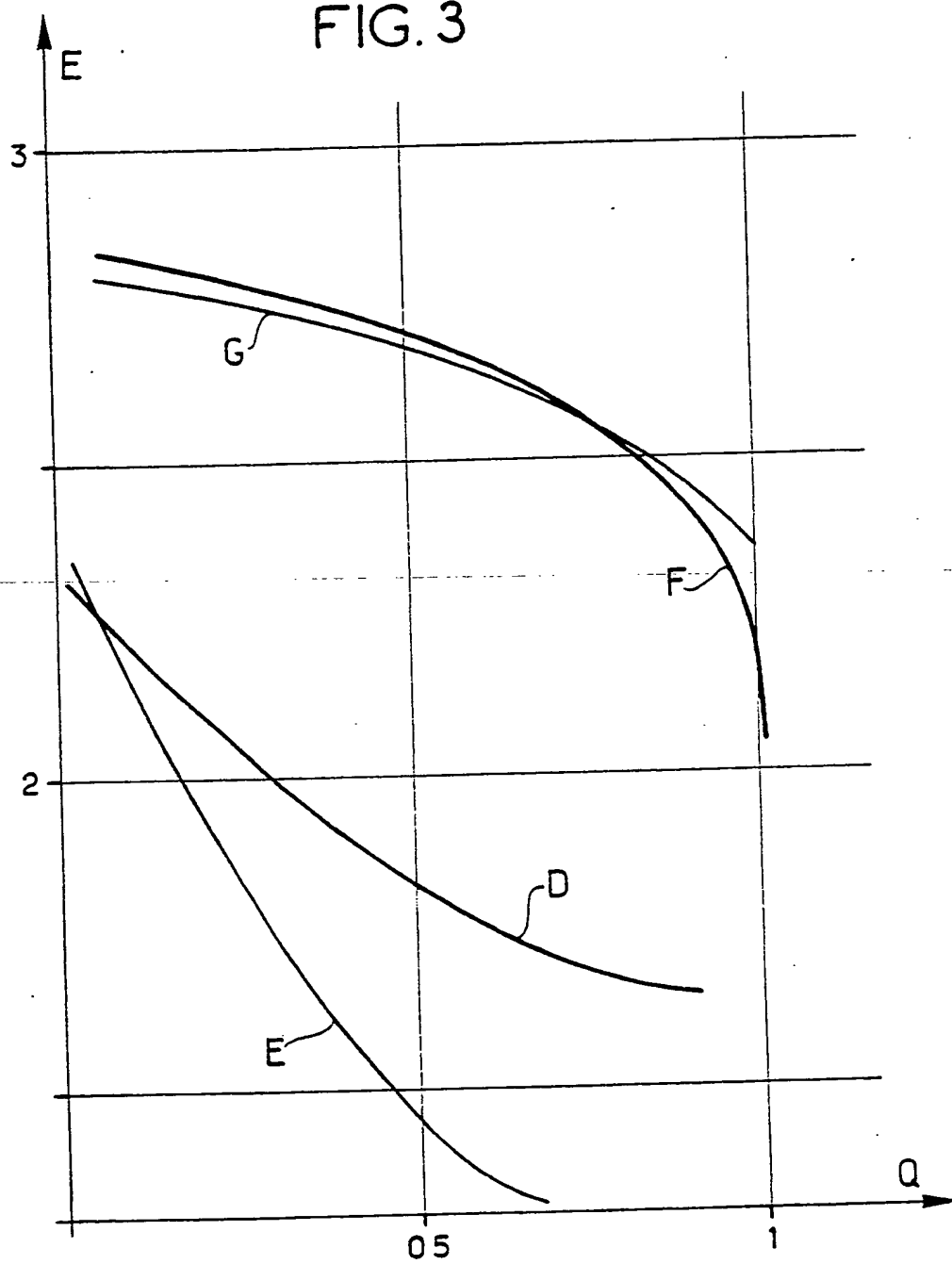


FIG. 3



## SPECIFICATION

## A lithium electric cell

5 The present invention relates to a lithium cell with a liquid organic electrolyte. 5

A number of surveys have been made during the past three years concerning the electrochemical insertion, or, rather, "intercalation" of lithium in two-dimensional inorganic compounds; there should be cited in particular the work of M.S. Wittingham, disclosed in US patent n° 4,049,879, as well as the surveys made by R. Brec and F. Le Méhauté, disclosed in French 10 patent n° 77 045 18. 10

These authors describe in particular compounds such as  $\text{TiS}_2$  and  $\text{NiPS}_3$  installed in the charged state in an electric cell as well as compounds of the  $\text{Li}_x\text{TiS}_2$  or  $\text{Ni}_x\text{PS}_3$  type used in the discharged state.

However, it has been observed that such compounds, as well as a number of inorganic 15 compounds cannot be directly synthesised by the dry method, since at their formation temperature, these compounds are not stable, but in contrast, they prove to be stable at ambient temperature. 15

Due to these considerations, research workers of Bell Telephone Laboratories have envisaged in particular stabilizing quadrivalent vanadium by producing  $\text{LiVS}_2$  initially, followed by electro- 20 chemical oxidation to remove the lithium. 20

Such work has also been disclosed in the article "Cathodes for non-aqueous  $\text{VS}_2$  based lithium batteries" on pages 825-850 of Vol 12 (1977) of the Material Research Bulletin.

The applicant has sought to produce new substances of high capacity and which remain stable even after a high number of charge/discharge cycles.

25 The present invention provides an electric cell which includes a positive electrode and a negative electrode in contact with a liquid electrolyte, said electric cell being characterized in that said positive electrode includes an active compound whose general formula is  $\text{Li}_x\text{Fe}_2\text{S}_z$  with 25  $x$  lying between 0 and 2 and  $z$  being not less than 3.

Examples of the invention are described by way of illustration with reference to the 30 accompanying drawings and graphs in which: 30

Figure 1 illustrates a button type electric cell in accordance with the invention; and

Figures 2 and 3 are graphs which illustrate the electrical performance of electric cells in accordance with the invention.

The applicant has developed a new positive electrode for an electric cell with a lithium 35 negative electrode. 35

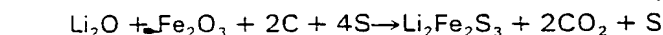
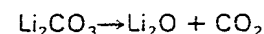
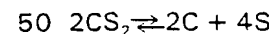
For that purpose, the applicant has produced improved ternary compounds, in particular of lithium, iron and sulphur in which the iron has a value which lies between 2 and 3, it being possible for such a compound to acquire, by limited electrochemical oxidation, an oxido-reduction state greater by about 1 than the preceding state and having a stable or metastable 40 state. 40

Such a compound is, in particular,  $\text{Li}_2\text{Fe}_2\text{S}_3$ .

The preparation method is as follows:

An intimate mixture of  $\text{Li}_2\text{CO}_3$  and  $\text{Fe}_2\text{O}_3$  is formed in stoichiometric proportions and is placed in an alumina boat which is placed in a quartz tube disposed in a furnace. The mixture is heated 45 to a temperature of  $800^\circ\text{C}$  while allowing argon which has bubbled through carbon bisulphide 45  $\text{CS}_2$  to pass through the tube for about 6 hours.

The mixture of  $\text{CO}_3\text{Li}_2$  and  $\text{Fe}_2\text{O}_3$  is sulphurized by nascent sulphur which results from the decomposition of the carbon bisulphide and as shown in the following reactions:



The compound  $\text{Li}_2\text{Fe}_2\text{S}_3$  can be determined quantitatively by a spectro-photometric absorption method and its presence in the form of a single phase is revealed by its X-ray spectrum which is set out in the table hereinbelow:

d(Å)	6.210	3.370	3.120	3.010	2.952	2.669	2.296	2.050	1.951
intensity	l	l	m	l	vl	m	m	H	l
d(Å)	1.899	1.773	1.741	1.627	1.520	1.339	1.114	1.062	
intensity	l	m	m	vl	vl	m	m	m	

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In the table,  
 l represents a low intensity  
 vl represents a very low intensity  
 m represents a medium intensity

15

15 H represents a high intensity.

Further, the spectrum allows the complete lack of the sulphides  $\text{Li}_2\text{S}$ ,  $\text{FeS}$ ,  $\text{FeS}_2$  to be detected. In other words,  $\text{Li}_2\text{Fe}_2\text{S}_3$  actually corresponds to a specific single phase.

It will further be observed that if the operating conditions—in particular the temperature—are varied, it is possible to obtain different compounds with a general formula of  $\text{Li}_2\text{Fe}_2\text{S}_z$  where

20

20  $3 \leq z < 4$ .

For example, for a temperature of  $650^\circ$ , the compound  $\text{Li}_2\text{Fe}_2\text{S}_{3.5}$  is obtained. The temperature may be varied generally between  $200$  and  $1000^\circ\text{C}$ . As the applicant has observed, such compounds are not reducible in the charged state to  $\text{FeS}$  or  $\text{FeS}_2$ . These substances are already used in electric cells.

25

25 In general, by a method similar to the one described above, it is possible to produce compounds whose general formula, as has been seen, is:  $\text{Li}_x\text{Fe}_2\text{S}_z$ .

These previously described compounds can therefore be used in electric cells with an alkaline negative electrode, as will be described hereinafter.

30

### 30 The positive electrode

The positive electrode includes said compound  $\text{Li}_x\text{Fe}_2\text{S}_z$  and in particular  $\text{Li}_2\text{Fe}_2\text{S}_z$ . Further, it may include other materials necessary to ensure good electronic conductivity or good contact with the collector, namely, carbon, graphite, copper, nickel, iron or a transition element.

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### 35 The negative electrode

The negative electrode includes an alkali metal and in particular lithium.

The collector must be made of metal which corrodes only slightly at the potential of the electrode.

By way of example, it would be possible to use an element in columns IVb, Vb, VIb, VIIb or VIII of the periodic table as well as copper, silver, zinc, aluminium or alloys thereof. Further, carbides, nitrides or borides of these compounds can be used.

40

### The electrolyte

45 The electrolyte includes an organic solvent which is stable with respect to the positive electrode and the negative electrode and in which the salt of an alkali metal, in particular lithium, is dissolved.

45

More precisely said solvent can be chosen from among propylene carbonate, dioxolane, dimethoxyethane, nitromethane, tetrahydrofuran and generally cyclic esters.

Said salt can be chosen from among perchlorates, hexafluoroborates, hexfluoroarsenates, nitrates, sulphates and methylchlorosulfonates.

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With reference to Fig. 1, a practical embodiment will now be given of a button type electric cell in accordance with the invention.

Fig. 1 shows the positive active mass 1, the negative active mass 2 and a porous separator 3 impregnated with electrolyte. References 4 and 5 denote, respectively, the positive collector in the form of a cup and the negative collector in the form of a cap.

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The positive active mass 1 (in the case,  $\text{Li}_2\text{Fe}_2\text{S}_3$ ) is compressed at a pressure of  $800 \text{ kg}$  in the cup 4 in a dry nitrogen atmosphere.

The negative active mass 2 (in this case, lithium) is compressed in argon in the cap 5. The separator 3 is of the cellulose type and is impregnated with electrolyte formed by  $1 \text{ M}$  propylene carbonate in which lithium perchlorate is dissolved. After crimping, the electric cell thus constituted is charged for  $80 \text{ hours}$  at  $200 \mu\text{A}/\text{cm}^2$ .

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Since the weight of the active material is  $66 \text{ mg}$ , its capacity is about  $8 \text{ mAh}$ .

Fig. 2 which is a graph of the electromotive force  $E$  in volts as a function of the discharged capacity  $Q$  in grams equivalent, shows, by means of curves A, B and C, the charge-discharge cycles of the above-described electric cell, at various currents, namely,  $100 \mu\text{A}$  for cycle A,  $780$

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$\mu\text{A}$  for cycle B and  $100 \mu\text{A}$  for cycle C.

In accordance with another embodiment, the positive mass 1 is  $\text{Li}_2\text{Fe}_2\text{S}_{3.64}$  and the negative mass 2 is lithium, the electrolyte being the same as previously. The cell is charged at  $200 \mu\text{A}/\text{cm}^2$ .

- 5 Fig. 3, which shows the same parameters as Fig. 2, gives the charge curve D and the discharge curve F of  $\text{Li}_2\text{Fe}_2\text{S}_{3.64}$  and the charge curve E and the discharge curve G of  $\text{Li}_2\text{Fe}_2\text{S}_3$ .  
 In accordance with yet another embodiment, the positive active mass 1 includes 66% of  $\text{Li}_2\text{Fe}_2\text{S}_3$  (or  $\text{Li}_2\text{Fe}_2\text{S}_{3.64}$ ) and 33% of acetylene black, the negative electrode being lithium.  
 Contrary to the previous examples, the positive mass 1 is not compressed in the cup 4, but  
 10 simply packed. In that case, less polarization is observed than in the preceding cases, the discharge voltage being stabilized at 2 volts at  $200 \mu\text{A}/\text{cm}^2$ .

Analogous results are obtained by forming a latex with the positive active mass by adding a binding agent such as polytetrafluoroethylene.

# 15 CLAIMS

1. An electric cell which includes a positive electrode and a negative electrode in contact with a liquid electrolyte, said positive electrode including an active compound whose general formula is  $\text{Li}_x\text{Fe}_2\text{S}_z$  with  $x$  lying between 0 and 2, and  $z$  being not less than 3.
2. An electric cell according to claim 1, wherein said active compound is  $\text{Li}_2\text{Fe}_2\text{S}_z$ .
- 20 3. An electric cell according to claim 2; wherein said active compound is  $\text{Li}_2\text{Fe}_2\text{S}_3$ .
4. An electric cell according to any preceding claim, wherein said positive electrode further includes a substance chosen from among carbon, graphite, copper, nickel, iron and any other transition element of the periodic table.
5. An electric cell according to any preceding claim, wherein the negative electrode  
 25 comprises an alkali metal, and particular lithium.
6. An electric cell according to any preceding claim, wherein said electrolyte includes an organic solvent in which a lithium salt is dissolved.
7. An electric cell according to claim 6, wherein said organic solvent is chosen from the group which includes propylene carbonate, dioxolane, dimethyloxyethane, nitromethane,  
 30 tetrahydrofuran and cyclic esters.
8. An electric cell according to claim 6, wherein that said salt is chosen from the group which includes perchlorates, hexafluoroborates, hexafluoroarsenates, nitrates, sulphates and methylchlorosulfonates.
9. An electric cell according to any preceding claim, wherein that the positive active  
 35 compound is prepared by successively: mixing a carbonate of lithium and an oxide of iron; and heating the mixture to a temperature which lies between  $200$  and  $1000^\circ\text{C}$  in a flow of inert gas; the inert gas preferably being argon which contains a compound of carbon and sulphur.
10. An electric cell substantially as herein described with reference to the accompanying drawings.

